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AN INVESTIGATION
OF A
MODIFIED BUNSEN ICE CALORIMETER

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ENTITLED Investigation of a Modified Bunsen-Ice Calorimeter

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INVESTIGATION OF A MODIFIED BUNSEN ICE CALORIMETER.

I Purpose. The purpose of the investigation was to test the action of a modified Bunsen Ice Calorimeter. Theory shows that the Bunsen Calorimeter is most promising for the determination of specific heat, but the results of the experiments are disappointing, because it appears that the instrument has defects. It was thought that the modified calorimeter might overcome one of these defects.

II Calorimetry. Calorimetry is the process of measuring the heat which a body emits or absorbs. The apparatus used in this process is called the calorimeter. Quantities of heat may be measured indirectly in a variety of ways, in terms of different effects of heat on material substances. The most important of these effects are change of temperature, transformation of energy and change of state.

The rise of temperature of a body, where heat is imparted to it, is found to be in general nearly proportional to the quantity of heat added. The thermal capacity of a body is measured by the quantity of heat required to raise its temperature one degree, and is necessarily proportional to the mass of the body for bodies of the same substance under similar conditions. The specific heat of a substance is sometimes defined as the thermal capacity of unit mass. The methods of measurement, founded on rise of temperature, may be classed as thermometric methods, since they depend on the observations of change of temperature

with a thermometer. The most familiar of these are the method of mixture and the method of cooling.

The method of mixture consists in imparting the quantity of heat to be measured to a known mass of water, or some other standard substance, contained in a vessel or calorimeter of known thermal capacity, and in observing the rise of temperature produced, from which data the quantity of heat may be found. This method is the most generally convenient and most readily applicable of calorimetric methods, but is not always the most accurate, because some heat is generally lost in transferring the heated body to the calorimeter, and some is lost when the calorimeter is raised above the temperature of its enclosure, and before the final temperature is reached.

A common example of the method of cooling is the determination of the specific heat of a liquid by filling a small calorimeter with the liquid, raising it to a convenient temperature, and then setting it to cool in an enclosure at a steady temperature, and observing the time taken to fall through a given range when the conditions have become fairly steady. The same calorimeter is afterwards filled with a known liquid, such as water, and the time of cooling is observed through the same range of temperature, in the same enclosure, under the same conditions. The ratio of the times of cooling is equal to the ratio of the thermal capacities of the calorimeter and its contents in the two cases. The advantage of the method is that there is no transference or mixture; the defect is that the whole measurement

depends on the assumption that the rate of loss of heat is the same in the two cases, and that any variation in the conditions, or uncertainty in the rate of loss, produces its full effect in the result, whereas in the previous case it would only affect a small correction.

The second general method of calorimetry, that based on the transformation of some other kind of energy into the form of heat, rests on the general principle of the conservation of energy, and on the experimental fact that all other forms of energy are readily and completely convertible into the form of heat. The two most important varieties of this method are mechanical and electrical. This, however will not be discussed further since it is not applicable to the present investigation.

The methods depending on change of state are theoretically the simplest, since they do not necessarily involve any reference to thermometry, and the corrections for external loss of heat and for the thermal capacity of the containing vessels can be completely eliminated. They, nevertheless, present peculiar difficulties and limitations, which render their practical application more troublesome and more uncertain than is usually supposed. They depend on the experimental fact that the quantity of heat required to produce a given change of state is always the same, and that there need be no change of temperature during the process. The difficulties arise in connection with the determination of the quantities of ice melted or steam condensed, and in expressing the latent heat of fusion or vaporization in terms of other units for

the comparison of observations. The earliest forms of ice-calorimeter were those of Black and of Laplace and Lavoisier.

a. Black's calorimeter (Figure 1) consisted of a block

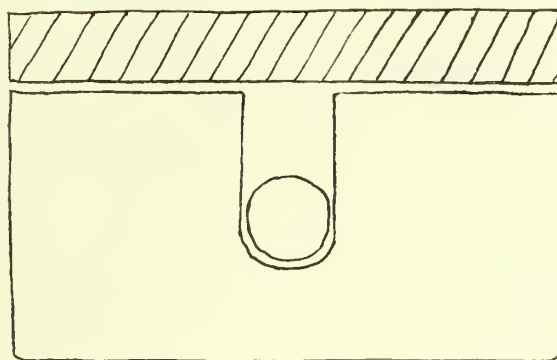


Figure 1

of ice in which a cavity was made, and which was provided with a cover of ice. The substance whose specific heat was to be determined was heated to a certain temperature, placed in the cavity, and allowed to remain there until it had attained a temperature of zero degrees. A weighed sponge was then used to wipe out all moisture. The increase of weight of this sponge obviously represented the ice which had been converted into water. By substituting data taken into a formula, the specific heat of the substance was computed.

b. Lavoisier and Laplace replaced the block used by Black in his experiments by a more complicated apparatus which was called the "ice calorimeter". (Figure 2). It consisted of

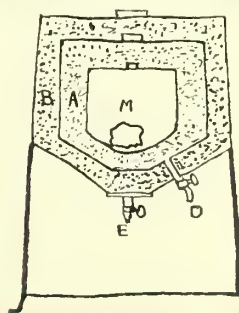


Figure 2.

three concentric tin vessels; in the central one was placed the body, M , whose specific heat was sought, while the other two were filled with pounded ice. The ice in compartment A was melted by the heated body, while the ice in compartment B cut off the heating influence of the surrounding atmosphere. The two stopcocks E and D gave issue to the water which arose from the melting of the ice. In order to find the specific heat of a body by this apparatus, its weight M is first determined; it is then raised to a given temperature, t , by keeping it for sometime in oil or water bath, or in a current of steam. Having been quickly brought into the central compartment, the lids are replaced and covered with ice as represented in the figure. The water which flows out by the stopcock D is collected. Its weight w , is manifestly that of the melted ice. The calculation is then made as in the preceding case.

The two calorimeters just described were not adapted for work of great precision, on account of the impossibility of accurately estimating the quantity of water left adhering to the ice in each case. This difficulty was overcome by the invention of Bunsen's ice calorimeter.

c. The Bunsen calorimeter was invented in 1870 by Robert Wilhelm von Bunsen, Professor of Chemistry at Heidelberg. The construction of the instrument is given as follows. (See Figure 3).

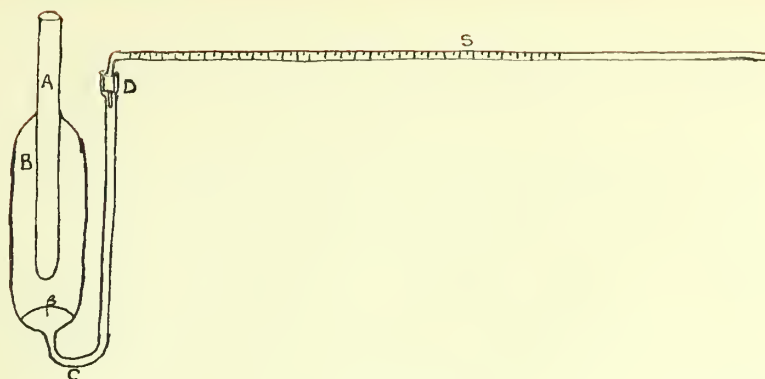


Figure 3.

A cylindrical test tube A was fused into a larger cylindrical glass bulb B which was furnished with a glass stem CD. This stem was filled with boiled mercury which also occupied the bulb to the level B. The remainder of the bulb B was filled with pure boiled water. A calibrated narrow glass tube S, furnished with a millimetre scale was fitted into a cork with fine sealing wax. Mercury was then forced into the tube S and, by adjusting the cork, could be placed at any convenient point.

In conducting the experiment the first operation was to freeze some of the water in bulb B. Two cylindrical semi tin plate vessels were partly filled with alcohol and connected by tubes to the test tube. These vessels were then put in a freezing mixture and by means of suction cold alcohol was passed to and fro and the bulb B reduced to the freezing point. It was necessary for the air freed water in B, to be reduced far below the normal freezing point before solidification set in, while the outside of the bulb became covered with a coating of ice, due to atmosphere. At last, where the temperature had been greatly reduced, the formation of ice suddenly began, and spread in a few seconds from the bottom of A to the top of B. Within these minutes the bulb was filled with thin plates and needles of ice, but from the

bottom of A to the level of the mercury below, the water was not frozen. By continued cooling a shell of solid ice was gradually formed around A from 3 to 10 mm. in thickness.

On account of the low temperature of the alcohol, the ice shell was much below zero, and if the instrument was not placed in snow at zero, a slow progressive freezing took place in the water for a long time. Boeser found that in this manner about 2 mcs. of water were frozen at the temperature of melting snow during the first seven hours and that this progressive freezing was sensible for one hundred and fourteen hours. After this time the whole apparatus had come to zero and freezing ceased. In order to interpret the indications of the instrument a known mass of water H, at a definite temperature t_1 , was introduced into the tube A. In falling to zero, this gave out a quantity of heat QH , and in consequence of the melting of ice, the mercury in the tube S receded through N divisions of scale. This gave the relation between the quantity of heat supplied in an experiment in tube A and the corresponding recession of mercury along the scale S, for if q is the quantity of heat corresponding to each division of scale:-

$$QH = qN$$

In determining the specific heat of any substance, a fragment was heated and dropped into the test tube which was partly filled with pure distilled water. This warmed the water at the bottom of the tube and tended to melt some of the ice which in turn caused the mercury to recede through N' divisions

on the scale. Hence if M' was the mass of the body, and Θ' its original temperature, the specific heat of the substance could be given by the equation

$$S = \frac{M'(\Theta - \Theta')}{M(\Theta' - \Theta)}$$

Bunsen, in a report to the Philosophical Magazine in March 1871, stated that the old instruments were not accurate because of the loss of so much liquid and heat. He made the following calculations for specific heat from his experiments.

Water	1.0000
Silver	0.0559
Zinc	0.0935
Antimony	0.0495
Cadmium	0.0548
Sulphur	0.1712

One of the chief difficulties encountered was the irregular movement of the mercury column due to slight differences in temperature. Professor C. V. Boys thought that he had greatly reduced this difficulty by the fusion of another cylindrical glass tube on the outside of the other two. He thought that by having the ice inside separated from the ice outside by an air space, the passage of heat would be greatly reduced. H. L. Callendar, in his report on Calorimetry in the Encyclopedia Britannica, stated that very good results were obtained by enclosing the calorimeter in a vacuum jacket which would practically eliminate conduction and convection. Radiation would also be reduced if the jacket were silvered inside. If the vacuum was really good, he said that

the external ice bath could be eliminated for the majority of purposes.

III Present Investigation. The accuracy of Bunsen calorimeter depends essentially on the care with which all the air has been expelled from the water enclosed by the bulb B (Figure 3a).

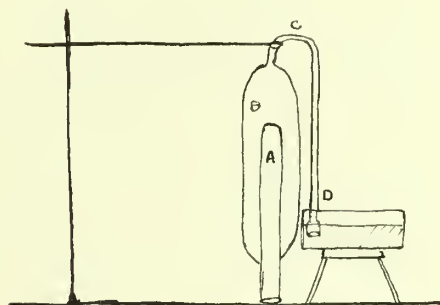


Figure 3a.

Dr. Preston in his book on "Heat" gave the following method for filling the instrument. The bulb is at first about half filled with water, and placed mouth downwards over a lamp, so that the water can be boiled, and the air expelled through the tube CD. During this process the mouth of the tube CD dips into a vessel of boiling water. When the water in the bulb has been boiled away to about $1/3$ of its original bulk the lamp is removed, and as the instrument cools the air free water is siphoned over into it through the tube CD from the vessel into which it dips. The instrument is now placed upright and the water siphoned out of CD, which is dried by an air current. The final filling-in of boiled mercury is done with a cannula, glass tube, so as to avoid the remaining of any air bubbles on the sides of the tube.

This method was followed at first but later changes

were made which makes the process more easily and quickly accomplished. A small quantity of distilled water was put into bulb B, which was heated to steam temperature, by the aid of the Bunsen Burner, and allowed to boil for several minutes. Air was expelled through the mouth of tube CD which had previously been put into a dish of boiled distilled water as described above. The flame was then taken away and as the vapor cooled and condensed a vacuum formed which brought water over into the bulb until it was about half filled. At this point the mercury was introduced in the tube by means of pouring, and the instrument put back onto a ring stand, with the mouth of CD into boiled distilled water as before, and boiled again. This time a great deal of air was expelled, both from the water and the mercury. It was assured after considerable boiling that the air was entirely expelled after which the bulb was allowed to fill with water as before. This was left over night in this same position.

A small bubble remained at the joint of tube CD which was brought to the surface D as the calorimeter was turned upright. CD was then filled with mercury by a process of pouring and pushing with a small iron wire.

See Photograph on page 102.



Barometer. In a Galilei thermometer.

Experimentation was first started with a calorimeter of the ordinary type made of pyrex glass. The process of freezing was much the same as described previously, except in the matter of the freezing mixture. The calorimeter was packed in shaved ice and several methods of freezing were tried. In the first attempt, a small quantity of ether was put into the test tube. Two tubes, which had been forced through a cork, were put down into the test tube (as shown in figure 4.)

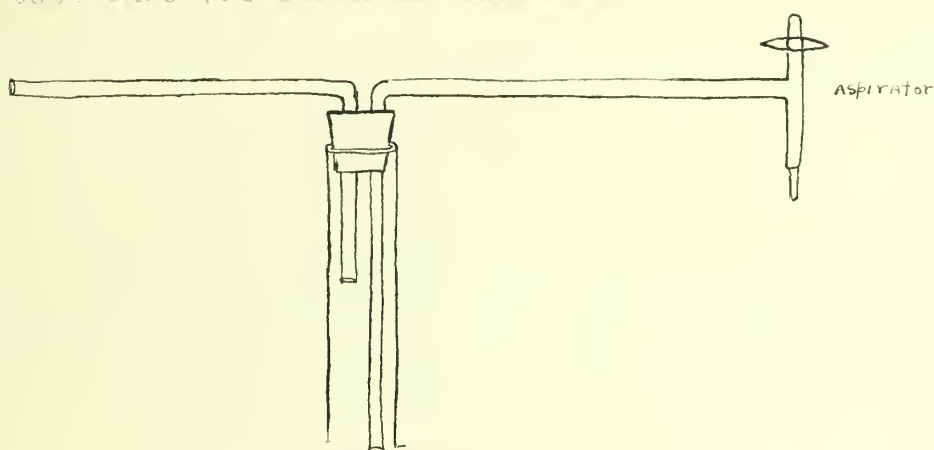


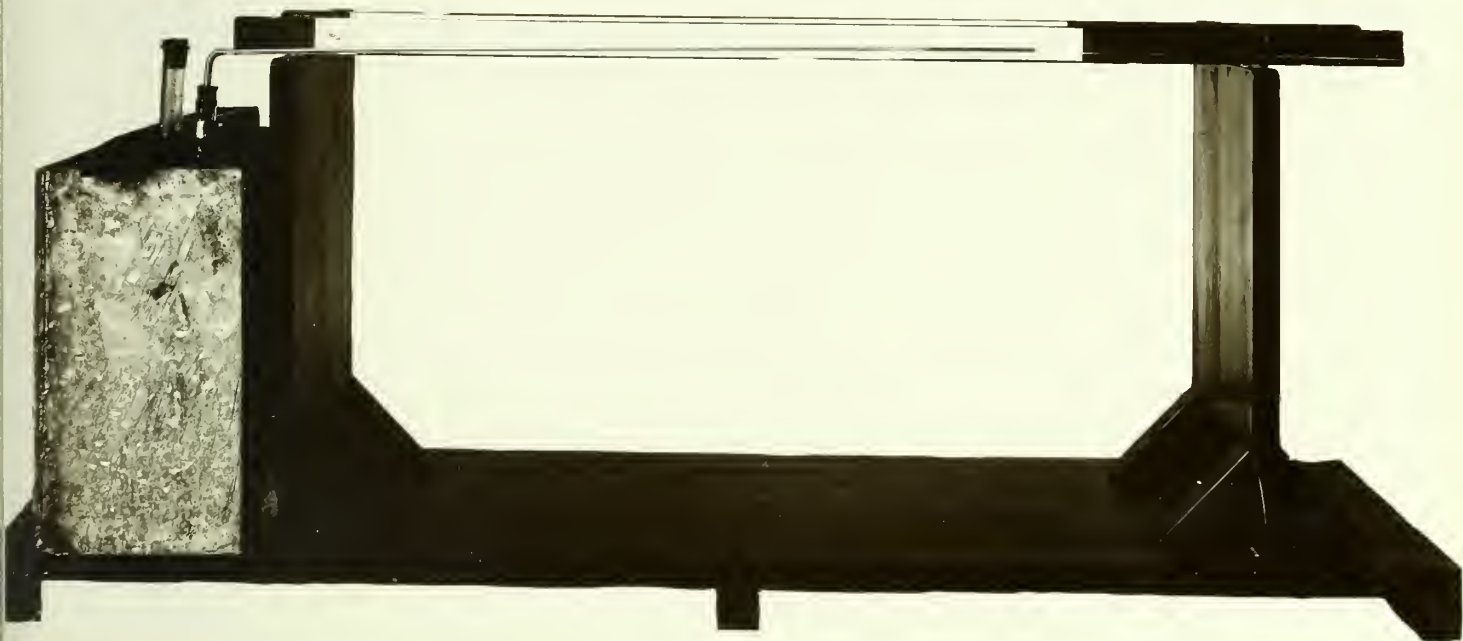
Figure 4.

The end of one of these tubes was then fastened to the aspirator, and the suction helped to evaporate the ether much in the same way that alcohol was used by Sorensen. This was repeated several times without success. This method was then abandoned and a mixture of ground calcium chloride and snow was used. This gave a temperature of -5°C , and froze a thin film of ice around the test tube, but the calcium chloride made a hard formation in the bottom of the tube that was almost impossible to remove. Finally a mixture of three parts ice and one part common salt (valerian) were used and found to give a temperature of -15°C . If larger

quantities were used the freeing was quicker and more satisfactory.

See photograph of page 12.

The specific heat of aluminum was then determined. The test tube was entirely filled with the mixture and allowed to stay there until it began to melt. This was siphoned out and test tube rinsed with ice water to prevent any formation of salt. It was again filled with the solution and this time the mercury fairly shot forth into S for four or five centimeters. This indicated that the ice was forming and the next time only two centimeters of ice and salt were put into the test tube. The mercury gradually crept forth in the tube S and this process was continued until the desired weight of ice was frozen. A small quantity of water at room temperature was then weighed and put into the tube. This caused the mercury to recede in the tube a few centimeters, and as soon as it reached 0° readings were taken. Next a small coil of aluminum wire, of known temperature and mass, was lowered into the test tube into which had also been poured enough water at 0° to cover the coil. The test tube was corked and the mercury tube observed. Sometimes the aluminum caused the mercury to recede and sometimes it did not but in



A photograph of the apparatus after it is set up ready for use, showing the box in which the calorimeter is packed in snow, and the capillary tube extending along the scale.

every instance, upon removing the calorimeter from the room, it was found that a pocket of water had been formed between the test tube and the mantle of ice. This showed that the heat given off from the water and the coil did not melt the ice clear through but only around the test tube.

DATA

	<u>First Trial</u>	<u>Second</u>	<u>Third</u>
Weight of Water	7.1381 gms.	5.6565	7.115 gms.
Weight of Aluminum	3.767	3.7441	3.7441
Distance of recession for Water	7.3 cm.	4.2 cm.	1.3 cm.
Distance of recession for Aluminum	1.6 cm.	1.9 cm.	1.2 cm.
Change of Temperature of Water	27.1° C.	24.5° C.	22.3° C.
Change of Temperature of Aluminum	27.5° C.	22.6° C.	22.0° C.
Calculated Specific Heat	.132	.63	.05

The results of the different trials are not concordant. This would appear to be due, at least in part, to the formation of a water pocket about the test tube on already explained. The pile of ice about this would tend to prevent a change in volume and a movement of the mercury column.

See photograph on page 18.

The modified calorimeter was thought to be so constructed as to correct this defect. It was made identical with the first one but with small platinum wires fused into the end of the test tube (as shown in Figure 5). It was thought that the heat



FIGURE 1. The C. of

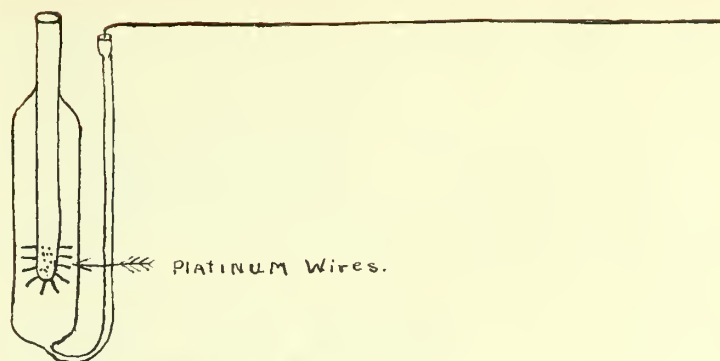


Figure 3.

would be conducted along these wires and cause the ice to form and melt at the wires, thus allowing a free change in the volume.

Tests with the modified calorimeter were not taken because no water last appeared where the wires were fused to the glass. The instrument maker was unable to complete a second one in time for this investigation.

IV Conclusion. During the course of the investigation, a method was developed for filling the calorimeter so as to expel the air, a satisfactory method of freezing was worked out and the pocket of water between the ice and the test tube was found as predicted. Therefore it seems very likely that the modified calorimeter will be an improvement.

The thanks of the Author are due to Professor F. R. Fuisen of the University of Illinois, who suggested the problem and who has given most helpful supervision during the course of the investigation, and to Miss Nellie F. Bates, her partner.

BIBLIOGRAPHY

1. W. S. Callender - "Calorimetry."
Encyclopaedia Britannica
Eleventh Edition - Volume 5, Pages.
2. Preston - "Theory of Heat"
3. R. Tansley - "The Ice Calorimeter"
Philosophical Magazine 1871, Volume XL, Page 161.
4. Garot's Physics - Page 448.
Translated from French by Mr. Atkinson.

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